

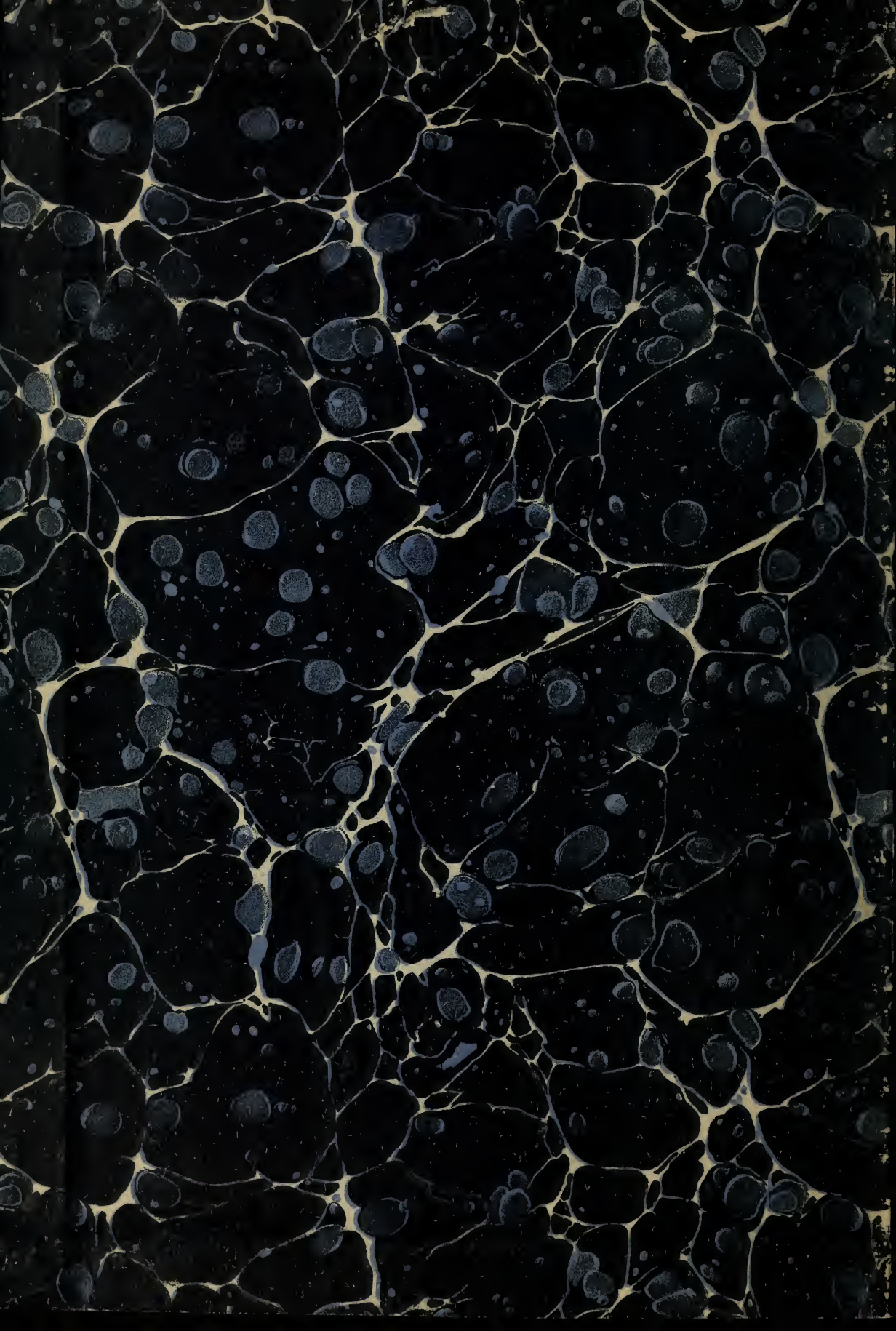
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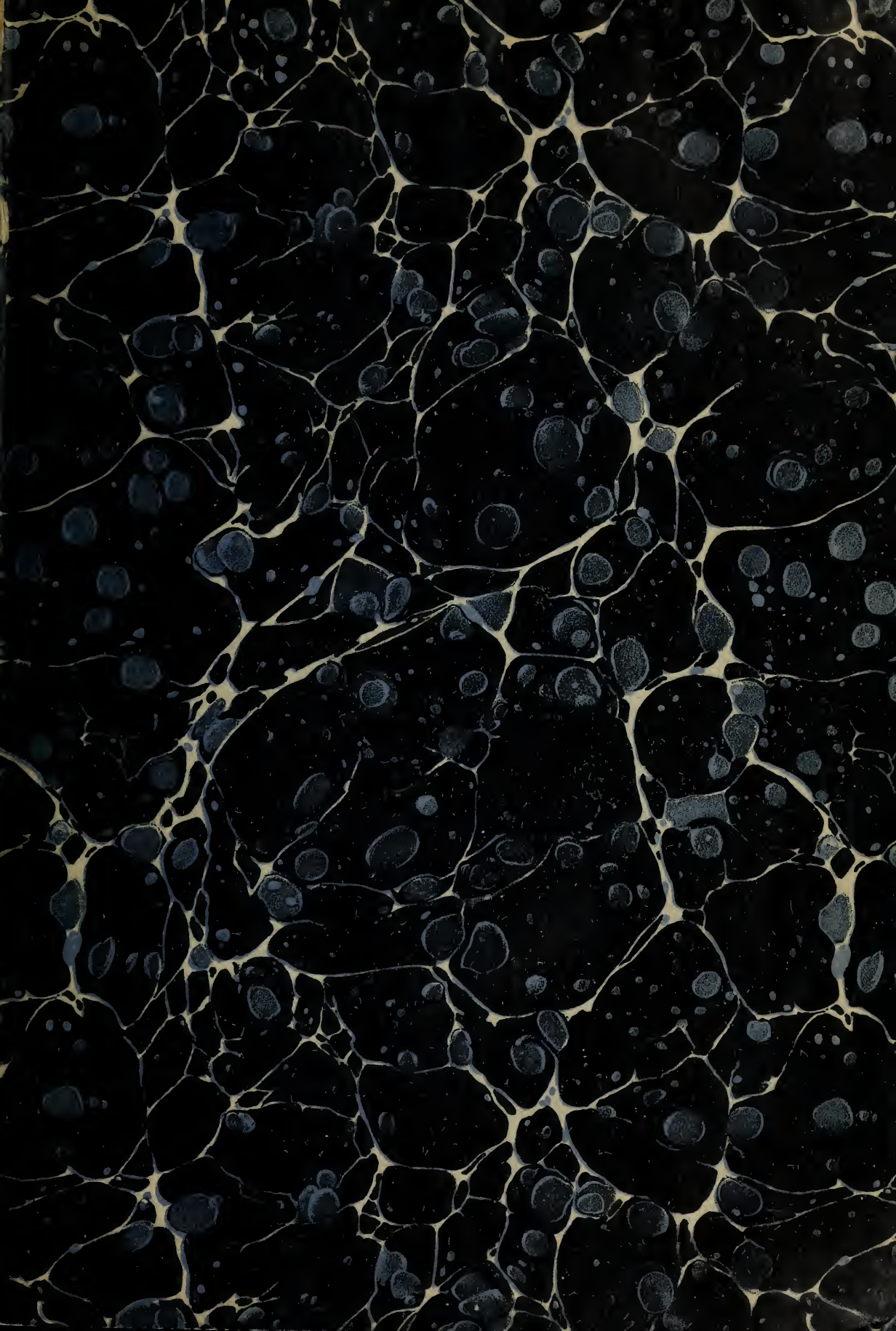
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DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

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S. W. STRATTON, DIRECTOR

No. 24

DETERMINATION OF PHOSPHORUS IN STEELS CONTAINING VANADIUM

BY

J. R. CAIN, Associate Chemist

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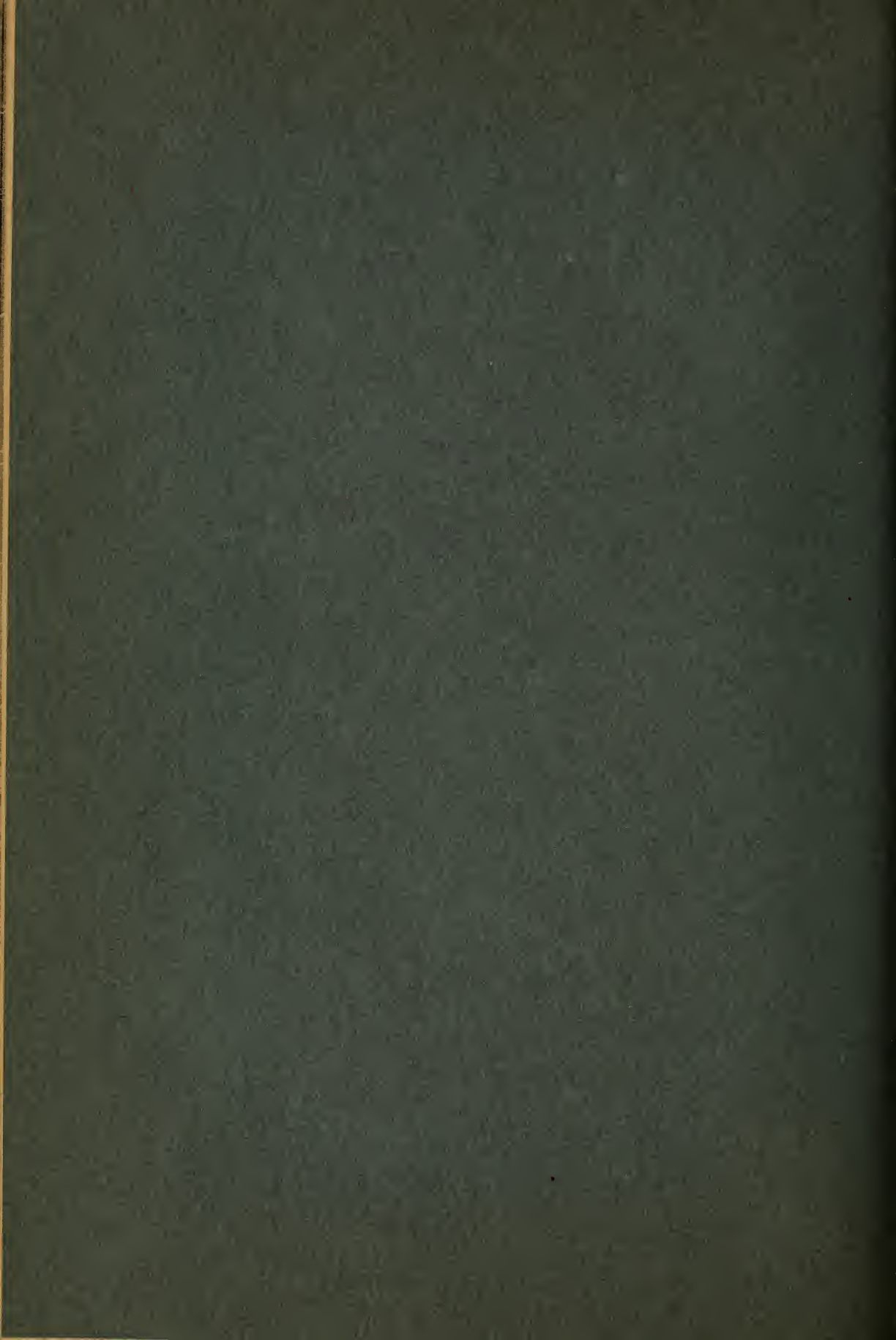
F. H. TUCKER, Assistant Chemist

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[MAY 17, 1913]



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DETERMINATION OF PHOSPHORUS IN STEELS CONTAINING VANADIUM

By J. R. Cain and F. H. Tucker

It is known that vanadic acid, even when present in small quantity, interferes with the precipitation of phosphorus as phosphomolybdate. Where the quantity of phosphorus is small relatively to the vanadium, as in steel, the vanadium not only contaminates the precipitate which is obtained, but also retards the rate at which it is formed and may prevent complete precipitation.

While developing a method in this laboratory for the determination of vanadium by coprecipitation with phosphomolybdate,¹ it was observed that the vanadium is precipitated in this manner only when present in the quinquivalent condition; quadrivalent vanadium was not precipitated, neither was pervanadic acid. In some experiments made by adding enough hydrogen peroxide to a solution containing vanadium to convert all of it to the pervanadate, not the slightest coprecipitation was observed with large or small amounts of added phosphate. The precipitates of phosphomolybdate obtained had the normal canary-yellow color, in contrast to the orange-red tint of precipitates containing vanadium. Other tests also showed no vanadium in such precipitates.

These observations suggested the possibility of determining phosphorus in the presence of vanadium by converting the latter to pervanadic acid before adding the molybdate reagent. To test this question, determinations of phosphorus in the B. S. Vanadium Standard (No. 24), in the B. S. Chrome-Vanadium Standard (No. 30), and in some synthetic solutions containing varying proportions of iron, chromium and vanadium, were carried out by the alkalimetric method, except that the vanadium was

¹ Cain and Hostetter: B. S. Tech. Paper No. 8; J. Ind. and Eng. Chem., 4, p. 250; 1912.

converted, before precipitation of the phosphorus, to pervanadic acid by means of hydrogen peroxide. While this method yielded satisfactory results with the majority of the large number of samples tested, there were occasional irregularities which we were not able to eliminate. In cases where the method failed the precipitates were red, the results were low, and no further precipitate formed after a long period of time. In a series of determinations with a given sample faulty results occurred only occasionally. A great deal of work was done in trying to find the causes of these apparently accidental failures by varying the concentration, temperature, acidity, etc., of the solutions, but without success.

Apparently the trouble is due to a decomposition of the hydrogen peroxide and of the peroxidized vanadium before complete precipitation of the phosphorus takes place, and this decomposition is probably caused by the presence of one or more of the numerous catalyzers which decompose hydrogen peroxide. Owing to this fact and to the further objection that hydrogen peroxide also peroxidizes the molybdenum of the precipitant, thereby causing possible abnormalities in the action of the latter, it was decided to abandon this method for general work. It is quite possible, however, that correct results on a given sample may be obtained by making several determinations and eliminating from the average those which are evidently wrong when judged by the criteria above indicated.

Experiments which resulted in the discovery of a satisfactory method based on reduction of the vanadium to the quadrivalent condition were then begun. The fact that phosphorus may be quantitatively precipitated by the molybdate reagent when present with vanadium in this condition² has long been known. We have found that the difficulty in applying this principle to the analysis of steel arises from the fact that whereas original solution of the metal must be made in nitric acid, if the direct molybdate precipitation is to succeed, the presence of this acid complicates the reduction of the vanadium as the operation is ordinarily carried out. It has often been attempted to reduce vanadium to the

² Treadwell: *Kurz. Lehrbuch der Analy. Chem.*, pp. 227 and 228, 4th Ed., Vol. 2; 1907.

quadrivalent state by means of ferrous iron, but the statements in textbooks referring to this method indicate, directly or indirectly, that success has not been attained. Thus, Johnson³ states, and gives results indicating that such reduction, as carried out in his experiments, did not give correct results for phosphorus. Brearley and Ibbottson⁴ give determinations on two samples of ferro-vanadium containing large amounts of phosphorus, where the vanadium had been reduced under conditions specified by them.

Whether or not the phosphorus content which they reported was correct can not be deduced from their statements, for this element was not determined by any other method known to give a correct result. It is equally impossible to decide from their experiments whether the vanadium was completely reduced at the time of precipitation. If it was not completely reduced (causing low results for phosphorus), there would have been produced a corresponding amount of the orange-colored precipitate which always forms in the presence of vanadic acid, but this, when associated with the large amount of normal phosphomolybdate which they obtained (their samples contained 0.65 per cent and 1.35 per cent phosphorus, respectively), might easily have escaped their notice. From other statements made by Brearley and Ibbottson on this subject⁵ it would appear that they believe the formation of an orange-colored precipitate has little significance in affecting phosphorus results, the deficiency in phosphorus precipitated in such cases being compensated by the positive error caused by the vanadium associated with the precipitate. In this connection it may be stated that our results show that formation of a red or orange-colored phosphomolybdate always indicates incomplete precipitation of the phosphorus.

Having confirmed, by a series of results, the fact that phosphorus is quantitatively precipitated as phosphomolybdate in the presence of quadrivalent vanadium alone, the disturbing factors operating when vanadic acid is reduced by ferrous iron in nitric-acid solutions of steels as a preliminary to the determination of phosphorus were investigated.

³ *Chemical Analysis of Special Steels, etc.*, pp. 22 and 23; 1909.

⁴ *The Analysis of Steel Works Materials*, p. 166; 1902.

⁵ *Loc. cit.*, p. 165.

Duplicate nitric-acid solutions of steel containing added vanadic acid were reduced with excess of ferrous sulphate. To one of the pair there was added the usual proportion of ammonia used in a regular phosphorus determination, and, after cooling, the color of the solution was compared with the companion solution to which no ammonia had been added. Not only had the blue color of the first solution due to reduced vanadium disappeared, being replaced by the yellow tint of vanadic acid, but the treated solutions usually gave but a slight test for ferrous iron. It thus appears that quadrivalent vanadium is oxidized by the nitric acid when the solution is heated by adding the necessary amount of ammonia. The vanadic acid thus formed would have prevented complete precipitation of phosphorus; moreover, most of the excess of ferrous iron, which would have tended to keep the vanadium reduced, had disappeared.

Solutions of steel containing vanadium and phosphorus were then prepared for precipitation of the latter by reducing with ferrous sulphate under the proper conditions to insure an excess of the reducing agent being present at the time of adding the molybdic reagent. When precipitation was made at 35° to 45° C, the solutions usually gave no test for ferrous iron after completion of the five-minute period of shaking generally recommended. When the reducing agent had thus disappeared, the oxidation of the hypovanadic acid was indicated by change in color of the solution, by abnormal color of the precipitate, and by low results. However, if precipitation was made at 15° C, excess of ferrous iron was almost always present.

We sought to determine whether phosphorus may be quantitatively precipitated as phosphomolybdate at low temperatures. With prolonged and thorough shaking or agitation of the solution, quantitative precipitation can be made at temperatures of 15° to 20° C, and our successful determinations, given in Table I, have been made at these temperatures. A 10-minute shaking suffices; the precipitate thus formed settles rapidly and filters as readily as that formed at 35° to 45° C in the ordinary procedure for determining phosphorus in steels.

Even with an excess of ferrous iron, as indicated by the ferri-cyanide drop test, red or orange-colored precipitates and low

results were often obtained. The solutions in such cases had a deep red color. There was a strong odor of oxides of nitrogen and sometimes even evolution of these gases. It was evident, then, that under certain conditions vanadic acid in nitric acid solution would not be completely reduced by ferrous iron, even with a considerable excess of the latter present. The trouble was found to be caused by the presence of oxides of nitrogen, due to interaction of ferrous iron and nitric acid; for when the gases were expelled from the solution, for instance by passing carbon dioxide in the cold for a sufficient time, the deep red color disappeared, the phosphorus precipitates were normal in color, and the results were quantitatively correct. To further test this point, a vanadate solution was reduced by sulphurous acid, the excess of reducer removed, and the vanadyl solution thus formed added to the nitric-acid solution of a vanadium-free steel. Oxides of nitrogen, formed during the solution of zinc in nitric acid, were passed into the solution thus prepared. A gradual disappearance of the blue color, due to reduced vanadium, was observed, and the phosphomolybdate precipitate obtained from the solution of the steel was orange colored, both results indicating that the oxides of nitrogen had caused oxidation of the vanadium. Some experiments were also made by precipitating phosphorus from steels containing vanadium, by reducing the latter with an excess of ferrous sulphate, the flask in which precipitation was made being filled with carbon dioxide; under these conditions there was complete precipitation and the phosphomolybdate had the normal color. It thus appears probable that the nitric oxide (NO) formed by action of the ferrous salt on nitric acid serves as a carrier of atmospheric oxygen to the vanadyl compound.

The method of preparing solutions of steels for phosphorus determination in the experiments described above was the usual one of dissolving in nitric acid of 1.135 specific gravity, oxidizing with excess of permanganate solution, and destroying the excess of oxidizer (with simultaneous partial or complete reduction of the chromic and vanadic acids in solution) by ferrous sulphate, sulphurous acid, or a sulphite. After the observations above noted had been made, it was finally found that, observing the

precautions shown to be necessary by the preceding experiments, samples in which the preliminary reductions of excess of permanganate, manganese dioxide, etc., were made with ferrous sulphate almost always gave trouble through incomplete precipitation, red or orange-colored precipitates, etc., whereas, on the other hand, samples in which this reduction was made by sulphurous acid or a sulphite nearly always gave good results. In the latter class of samples, also, after addition of ferrous sulphate to complete the reduction of the vanadium before adding the molybdate reagent, no odor of nitrous fumes was noticeable. Experiments were then made with the idea of reducing the vanadium by sulphurous acid alone, without the use of ferrous salt at all. This can be done; the essential conditions are to keep the temperature of the solution low and to allow time enough. Phosphomolybdate precipitated from such solutions has the normal color, and precipitation is quantitative. On account of the long time necessary, however, reduction by sulphurous acid alone is not to be recommended for routine work.

Our conclusion, then, is that the presence of small amounts of sulphurous acid in the solutions where that reagent was used as a reducing agent for destroying permanganate, etc., counteracted the effect of, or prevented the formation of, oxides of nitrogen upon adding ferrous salt. The formation of these oxides being thus avoided, their effect in preventing complete reduction of vanadic acid by ferrous salt was eliminated, and hence correct results could be obtained for phosphorus.

As a result of these investigations, then, the following four conditions should be observed in precipitating phosphomolybdate in nitric-acid solutions of steels containing vanadium by the method of reduction of the vanadium to the quadrivalent state:

(1) The temperature of precipitation should be held at a point (15° to 20°) where the nitric acid does not oxidize the excess of ferrous salt or the reduced vanadium before complete precipitation of phosphorus takes place; (2) the partial neutralization with ammonia, frequently used when phosphorus is precipitated as phosphomolybdate, must be made before reduction of the vanadic acid, otherwise the heat of neutralization causes reoxidation of most of the ferrous iron and reduced vanadium by the nitric acid;

(3) care must be taken to prevent the action of oxides of nitrogen, formed by interaction of ferrous salt and nitric acid, on the reduced vanadium; since these substances seem to catalyze the oxidation of the vanadyl salt and may in some cases completely prevent precipitation of the phosphorus, owing to the large amount of vanadic acid so produced; (4) efficient means for shaking or agitation of the solutions in which precipitation is to take place must be provided. A fifth condition, not likely, however, to give trouble with ordinary care, is the avoidance of too great an excess of ferrous salt. Under certain conditions, not fully investigated by us, a large excess of ferrous iron in the presence of vanadic and molybdic acids causes reduction of the latter, which, of course, is to be avoided for the present purpose. When all these conditions are observed there is no coprecipitation of vanadium in solutions containing as high as 1.5 per cent of this element. This point was verified by testing phosphomolybdate precipitates (from a steel containing 0.112 per cent phosphorus and 1.5 per cent vanadium) for vanadium by dissolving the precipitates in concentrated sulphuric acid, adding a drop or two of nitric acid and heating till fumes were given off strongly; on cooling no yellow color developed, showing that no vanadium had been coprecipitated.⁶

The method, which is described below, is adapted to any steel containing vanadium, no other element which ordinarily complicates the determination of phosphorus being present. If tungsten, titanium, arsenic, tin, etc., are present, their disturbing influence is eliminated by the usual methods for steels containing no vanadium. Nickel, copper, chromium, molybdenum, or aluminum, when present as alloying elements along with the vanadium, do not interfere. The details of the method are as follows: The solution of the steel, up to the point where precipitation of the phosphorus is to be made, is prepared as for an ordinary phosphorus determination by the alkalimetric method, viz, solution of 1 to 2 grams in 100 cc of nitric acid (specific gravity 1.135), oxidation with slight excess of permanganate solution while boiling, destruction of the excess of permanganate, etc., by a slight excess of sulphur dioxide or a sulphite, cooling of the solution

⁶ Cain and Hostetter, loc. cit.

and addition of 40 cc of ammonia (specific gravity 0.96). Any steel which does not give all its phosphorus to the solution by this method must be treated in an appropriate manner, so that the acidity, concentration of ammonium nitrate, and total volume obtained are always the same as by the method of solution directed. Slight deviations from these conditions are, however, probably without significance. Assuming solution of the steel and partial neutralization to have been made as directed, the solution is cooled to 15° to 20° C, and 5 cc of a saturated solution of ferrous sulphate and two to three drops of concentrated sulphurous acid are added. After addition of 40 cc of molybdate reagent the solution is shaken in an efficient manner for 10 minutes. The precipitate, after settling (which is quite rapid), is then filtered off, washed in the usual manner, and titrated by the alkali-metric method.

The following table gives results by this method on synthetic solutions made with B. S. standard acid open-hearth, basic open hearth, and Bessemer steels, of varying phosphorus and carbon content, to which vanadium was added as sodium vanadate and chromium as chromium nitrate. The acid and alkali solutions used for titrations were standardized against B. S. standard steels No. 19a (A. o. H. 0.2) and No. 9a (Bes. 0.2 renewal). The individual determinations in each series are single determinations only; the good agreement in all cases with the certificate values for phosphorus of the individual steels shows the reliability and accuracy of the method.

TABLE 1

B. S. steel standards	Vana- dium present, per cent approx- imately	Chro- mium present, per cent approx- imately	Phos- phorus present, per cent (certifi- cate value)	Phosphorus found with—		Differences (in per- centages on steel) with—	
				V. present	V.+Cr. present	V. present	V.+Cr. present
V. steel No. 29.....	$\left\{ \begin{array}{l} .15 \\ .15 \end{array} \right.$	0.035	0.037	+0.002
				.038	+ .003
Cr. V. steel No. 30.....	$\left\{ \begin{array}{l} .21 \\ .21 \end{array} \right.$	$\left\{ \begin{array}{l} 1.35 \\ 1.35 \end{array} \right.$.043	0.046	+0.003
					.048	+ .005
	.2	.5	.0082	.007	.008	— .001	— .000
	.4	1.0008	.007	— .000	— .001
B. O. H. 0.2 C. Renewal 11a....	.6	2.0008	.006	— .000	— .002
	.8	3.0008	.010	— .000	+ .002
	1.0	4.0007	.008	— .001	— .000
	.2	.5	.0246	.024	.023	— .001	— .002
	.4	1.0025	.022	+ .000	— .003
B. O. H. 0.8 C. Renewal 14a....	.6	2.0024	.024	— .001	— .001
	.8	3.0023	.024	— .002	— .001
	1.0	4.0023	.022	— .002	— .003
	.2	.5	.045	.044	.046	— .001	+ .001
	.4	1.0046	.047	+ .001	+ .002
B. O. H. 1.0 C. Renewal 16a....	.6	2.0044	.047	— .001	+ .002
	.8	3.0046	.050	+ .001	+ .005
	1.0	4.0049	.044	+ .004	— .001
	.2	.5	.084	.087	.085	+ .003	+ .001
	.4	1.0084	.083	.000	— .001
A. O. H. 0.2 C. Renewal 19a....	.6	2.0084	.083	.000	— .001
	.8	3.0086	.084	+ .002	.000
	1.0	4.0084	.083	.000	— .001
	.2	.5	.112	.106	.109	— .006	— .003
	.4	1.0111	.117	— .001	+ .005
B. O. H. 0.2 C. Renewal 9a.....	.6	2.0111	.109	— .001	— .003
	.8	3.0110	.116	— .002	+ .004
	1.0	4.0106	.106	— .006	— .006

⁷ Certificate values.

The time required is practically that for determining phosphorus in an ordinary steel.

WASHINGTON, May 17, 1913.



